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SYNTHESIS AND DEFECT STRUCTURE OF $SrLa_2(Mg_2W_2)O_{12}$ AND $Sr_2La_2(MgW_2)O_{12}$

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$SrLa_2(Mg_2W_2)O_{12}$ crystallizes in an orthorhombic perovskite structure, showing a NaCl-type ordering as well as an ordering of A-site vacancies, whereas $Sr_2La_2(MgW_2)O_{12}$ has a 12-layer hexagonal structure with octahedral-site vacancies. This indicates that the formed structures are closely related to the sites where cation vacancies occur.

According to the previous work$^{1)}$, a new perovskite $La_{2.67}(Mg_2W_2)O_{12}$ has an orthorhombic multiple-cell with a=7.8157(5) Å, b=7.8344(6) Å and c=2 x 7.9067(6) Å. The superstructure is due to a NaCl-type ordering of the B ions as well as an ordering of A-site vacancies. Generally the B-site vacancies in the perovskites are unlikely to occur, except the ordered perovskites of $Ba_2(Y_{2/3}W)O_6$ type$^{2)}$. Hexagonal stacking polytypes with octahedral-site vacancies, however, have been known in some compounds such as 5-layer $Ba_5Ta_4O_{15}$$^{3)}$, 9-layer $Ba_3Re_2O_9$$^{4)}$ and 12-layer $Ba_4(CoRe_2)O_{12}$$^{5)}$. The structural information suggests how vacancy-site can be tolerated in the cationic lattice. In this connection it is of importance to study the formation mechanism of vacancy-sites through perovskite-type compounds derived from $La_{2.67}(Mg_2W_2)O_{12}$. An attempt to synthesize $SrLa_2(Mg_2W_2)O_{12}$ and $Sr_2La_2(MgW_2)O_{12}$ resulted in the formation of structurally different phases, which serves this purpose. The present paper describes the preparation and defect structure of both compounds.

The title compounds were prepared from $SrCO_3$, La_2O_3, MgO and WO_3 of high purity. The stoichiometric mixtures of the reagents were fired at 1200°C for 6 h in air. The reacted mixtures were further ground, hand-pressed into disks and refired twice at 1300°C for 6 h. The X-ray diffraction analysis of the products showed that the phases were well crystallized and that they did not contain any additional compound. The lattice constants were accurately measured by scanning at (1/8)° 2θ/min and were refined by a least-squares computer program.

The X-ray data for $SrLa_2(Mg_2W_2)O_{12}$ are given in Table 1. The powder pattern was very similar to that of $La_{2.67}(Mg_2W_2)O_{12}$ in general features. The additional reflections to quadruple the c-axis of perovskite subcell, although appeared in

Table 1. X-ray diffraction data for $SrLa_2(Mg_2W_2)O_{12}$

hkl	$d_{obs.}$	$d_{cal.}$	$I_{obs.}$	hkl	$d_{obs.}$	$d_{cal.}$	$I_{obs.}$
001**	7.88	7.89	11.0	133*	1.805	1.806	9.3
111*	4.53	4.54	46.5	313*		1.805	
002	3.94	3.95	4.3	331*	1.801	1.801	
020	3.92	3.93		024	1.763	1.763	1.2
200		3.92		204		1.763	
021**	3.51	3.52	8.7	042	1.759	1.759	
201**		3.51		240	1.756	1.756	
112**	3.22	3.22	0.3	402		1.756	
022	2.781	2.784	100.0	420	1.754	1.754	
202		2.781		241**	1.713	1.714	2.4
220	2.774	2.775		421**	1.712	1.712	
003**	2.630	2.631	3.4	224	1.608	1.608	41.1
221**	2.618	2.618		242	1.604	1.605	
113*	2.376	2.377	23.6	422		1.603	
131*	2.368	2.370		043**	1.573	1.574	0.8
311*	2.364	2.366		403**		1.572	
222	2.269	2.270	1.9	115*	1.518	1.518	8.9
023**	2.186	2.186	0.7	333*	1.513	1.513	
203**		2.185		151*	1.512	1.512	
004	1.972	1.973	39.8	511*	1.509	1.509	
040	1.963	1.965		025**	1.465	1.465	1.9
400	1.959	1.960		205**		1.464	
223**	1.909	1.909	4.4	044	1.392	1.392	18.0
041**	1.905	1.906		404	1.391	1.391	
401**		1.902		440	1.388	1.388	

* Superstructural reflection due to a NaCl-type ordering.

** Superstructural reflection due to an ordering of A-site vacancies.

Table 2. X-ray diffraction data for $Sr_2La_2(MgW_2)O_{12}$

hkl&	$d_{obs.}$	$d_{cal.}$	$I_{obs.}$	hkl&	$d_{obs.}$	$d_{cal.}$	$I_{obs.}$
003	8.89	8.87	1.6	0210	1.791	1.791	2.3
101	4.76	4.77	26.1	0114	1.769	1.769	22.5
006	4.43	4.43	18.5	214	1.765	1.765	
104	3.91	3.92	6.4	2011	1.712	1.712	3.8
107	2.989	2.990	100.0	217	1.649	1.650	29.0
110	2.796	2.797	66.8	030	1.615	1.615	16.7
018	2.741	2.742	5.1	128	1.604	1.604	
021	2.412	2.412	2.8	0213	1.563	1.563	2.7
116	2.365	2.366	12.9	306	1.517	1.517	4.3
1010	2.332	2.332	3.7	2110	1.509	1.508	
024	2.275	2.276	3.4	1115	1.496	1.498	16.4
0012	2.217	2.217	4.3	2014	1.495	1.495	
205	2.204	2.205		0117	1.490	1.489	
0111	2.164	2.164	7.2	0018	1.479	1.478	1.6
027	2.042	2.043	44.7	1211	1.461	1.460	3.7
1013	1.885	1.885	3.6	220	1.399	1.399	11.0
211	1.827	1.827	3.5	2113	1.365	1.365	2.6

& hkl with four numbers have 1 index greater than 9.

$La_{2.67}(Mg_2W_2)O_{12}$, were not observed in the X-ray pattern. All the reflections in Table 1 could be indexed as an orthorhombic cell with a=7.841(1) Å, b=7.858(1) Å and c=7.893(1) Å. Hence the reflections not marked by asterisks appear referring to a perovskite subcell. The superstructural reflections marked by an asterisk arise from a NaCl-type ordering of Mg^{2+} and W^{6+} ions in the octahedral sites, since they have either all odd or all even indices. In addition, the superstructural reflections marked by double asterisks arise from an ordering of A-site vacancies on alternate c-planes, since they occurred only when h+k=2n for (hkl) planes. Thus the superstructure of $SrLa_2(Mg_2W_2)O_{12}$ is shown in Fig. 1. The A-site vacancies are randomly distributed only to half of the A-sites in alternate c-planes.

The c/a ratio (1.006) of $SrLa_2(Mg_2W_2)O_{12}$ was smaller than that (1.012) of $La_{2.67}(Mg_2W_2)O_{12}$, in contrast with nearly equal b/a ratio (1.002). This may be related to higher occupancy probability of A-site ions in $SrLa_2(Mg_2W_2)O_{12}$. Because the pseudotetragonal distortion in these compounds arises from the ordering of the A-site vacancies along the c-axis, and the incomplete occupancy of the A-sites leads to the antiparallel displacement of B ions for the c direction.$^{6)}$

The X-ray data for $Sr_2La_2(MgW_2)O_{12}$ are given in Table 2. This pattern were similar to that of 12-layer $Ba_4(CoRe_2)O_{12}$$^{5)}$ belonging to space group R$\bar{3}$m, except relative intensity and systematic shift in 2θ. All the reflections observed could be entirely indexed as a hexagonal cell with a=5.5943(5) Å and c=26.606(3) Å. The c/a ratio approximates a 12-layer stacking sequence of AO_3 layers. This pattern obeyed the rhombohedral absence rule, -h+k+l=3n. Consequently $Sr_2La_2(MgW_2)O_{12}$ is concluded to have the same layered structure as $Ba_4(CoRe_2)O_{12}$. The ordered arrangement shown in Fig. 2 can be proposed on the basis of a crystallochemical similarity between the both compounds. The Mg^{2+} ions are occupied in the octahedra which share

● Sr^{2+} or La^{3+} ion
◑ Vacancy, Sr^{2+} or La^{3+} ion
⊙ Mg^{2+} ion
⊘ W^{6+} ion

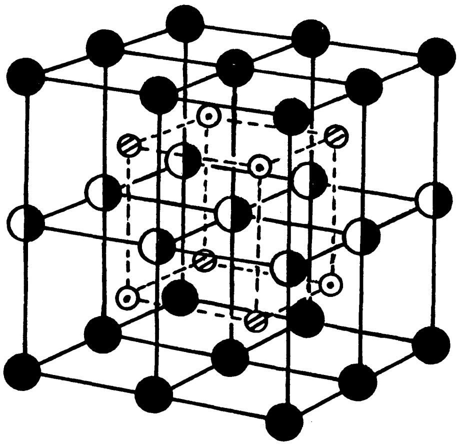

Fig. 1. Superstructure of $SrLa_2(Mg_2W_2)O_{12}$. Oxygen ions are not shown.

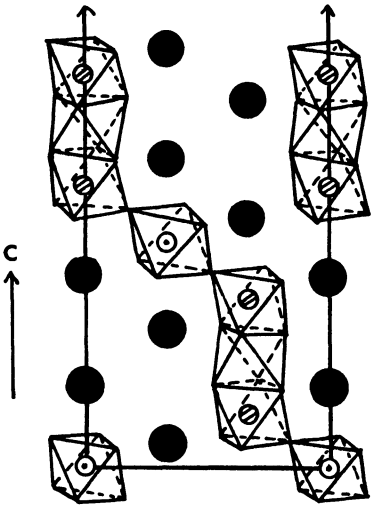

Fig. 2. 12-layer hexagonal structure of $Sr_2La_2(MgW_2)O_{12}$. Ions shown lie in the (110) plane. Only eight layers are shown, and repetition occurs after twelve layers.

corners only, and the W^{6+} ions are occupied in three face-shared octahedra which interpose a vacant octahedron.

The analogous Ni and Zn compounds were isostructural with $Sr_2La_2(MgW_2)O_{12}$. Their lattice constants were a=5.5904(2) Å and c=26.548(2) Å for $Sr_2La_2(NiW_2)O_{12}$, and a=5.6170(2) Å and c=26.610(1) Å for $Sr_2La_2(ZnW_2)O_{12}$, respectively.

Attempts to prepare B-deficient perovskite solid solutions between perovskite $Sr_4(M^{2+}{}_2W_2)O_{12}$[7,8] and hexagonal $Sr_2La_2(M^{2+}W_2)O_{12}$ with M=Mg or Ni were unsuccessful. This indicates that cation vacancies are unlikely to occur at the B sites.

Despite a slight difference in Sr- and Mg-components, $SrLa_2(Mg_2W_2)O_{12}$ was the ordered perovskite with A-site vacancies, whereas $Sr_2La_2(MgW_2)O_{12}$ was the 12-layer hexagonal compound with octahedral-site vacancies. It is significant in that this result showed a tendency for the formed structures to depend on the vacancy-site: The deficiency in A ions leads to the perovskite structure, while the B-ion deficiency prefers the hexagonal layered structure.

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